

## □ ANOMALY OF STRONG ELECTROLYTES

Oswald's dilution law gives satisfactory results only with weak electrolytes, whereas it does not hold good for strong electrolytes. In the case of strong electrolytes, the value of equilibrium constant ( $K$ ), instead of remaining constant, rapidly falls with dilution. The reason for the failure of the law may be sought in one or more of the following factors.

- (1) Most salts are ionic in nature even in the solid state and should be taken as completely ionic in the fused or dissolved state.
- (2) Arrhenius theory assumed free motion for ions, but this could be restricted by attraction between oppositely charged ions and between ions and polar solvent molecules.
- (3) The ions may get solvated and may thus affect the active mass.
- (4) As concentration in the case of strong electrolytes is very high, therefore, the presence of charge on the ions affects the equilibrium.

(5) As described above, the degree of ionisation was calculated from the value of  $\frac{\lambda_v}{\lambda_\infty}$ . In fact,  $\alpha$  cannot be accurately determined as such, because  $\frac{\lambda_v}{\lambda_\infty}$  gives only the conductivity ratio, not the degree of ionisation.

A number of following formulae have been suggested to explain the anomaly of strong electrolytes, but none of them has been found to be satisfactory.

Walker : 
$$\frac{\alpha^2}{(1-\alpha)V} = K \frac{(1-\alpha)}{\alpha}$$

van't Hoff : 
$$K = \frac{\alpha^{2/3}}{(1-\alpha)V^{1/2}}$$

Kohlrausch : 
$$K = (\lambda_\infty - \lambda_v)V^{1/2}$$

## □ DEBYE-HUCKEL THEORY

The quantitative aspect of the interionic attraction theory of electrolytic conductivity was developed by Debye and Huckel in 1923 and is known as Debye-Huckel theory of strong electrolytes, which can satisfactorily explain their behaviour in very dilute solutions, say below 0.005M. The postulates of Debye-Huckel theory are :

- (i) Every strong electrolyte is completely ionised at all dilutions.



CHEMISTRY

(ii) Two forces act on the mobile ions, viz; (a) electrical forces and (b) resistance due to viscosity of the medium, i.e., viscous drag.

∴ Resultant force = Electrical force - Viscous drag.

The velocity of the ions depends upon the magnitude of the resultant force.

(iii) The forces acting between the ions are electrostatic forces governed by Coulomb's law, according to which

$$F \propto \frac{q_1 q_2}{r^2}$$

where,  $q_1$  and  $q_2$  = charges on the ions and  $r$  = distance between the two ions.

(iv) Each ion is surrounded by a number of oppositely charged ions. Such an atmosphere is known as **ionic atmosphere**. Therefore, in the neighbourhood of a negative ion there will be more of positive ions than negative ions—as shown in figure (1). The following two factors tend to decrease the conductivity in concentrated solutions.

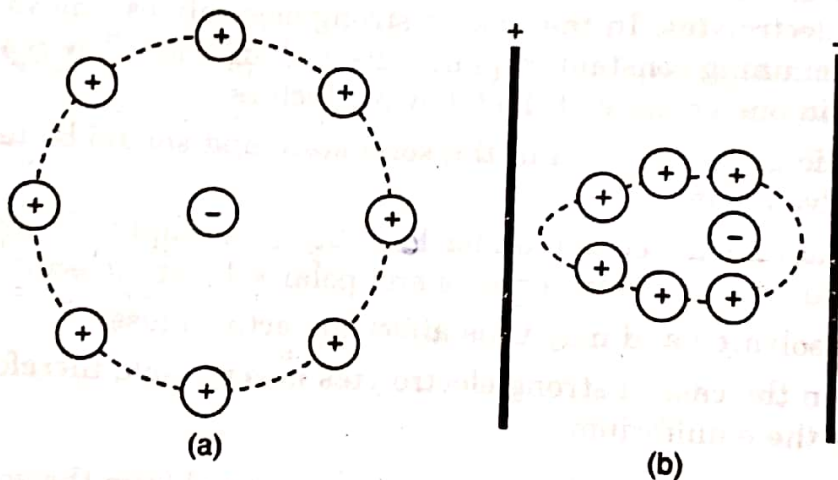


Fig. 1. Ionic atmosphere.

(a) **Relaxation effect.** Consider an anion surrounded by an ionic atmosphere of cations. Under the influence of electric field, the anion will move towards the anode, leaving behind the ionic atmosphere of the cations. As the anion moves, a new ionic atmosphere is under formation. But the new ionic atmosphere is not formed at the same rate as the old ionic atmosphere decays and hence the latter lags behind. A definite time is required for the new ionic atmosphere to build up, while the old ionic atmosphere is decaying. This lag of time is known as '**relaxation time**'. In other words, when a stress is applied, it takes a finite time for the atmosphere to relax, or to be re-established. Due to this time factor there will always be an excess of positive ions on the left of the ion and they will exert a retarding effect. The E.M.F. applied tends to move the ionic atmosphere in a direction opposite to the direction of the motion of the ion and this causes extra retardation of the velocity of the ions. The ionic atmosphere during the motion of the central ion becomes unsymmetrical. This effect on the velocity of the ion is called **asymmetry effect** or **relaxation effect**.

(b) **Electrophoretic effect.** Each ion is associated with some molecules of the solvent. Under the influence of electric field the ions start moving to the oppositely charged electrodes, which causes frictional resistance. Thus, the velocity of the ions decreases. The effect is known as **electrophoretic effect**, because of its resemblance with the phenomenon of electrophoresis exhibited by colloidal particles under the influence of electric current.

Debye and Huckel found that both these effects were proportional to the square root of the concentration of the electrolytes. According to them,



$$\lambda_v = \lambda_{\infty} - Kc^{1/2}$$

where  $K = \text{constant}$  for a given solvent and depends on the viscosity and dielectric constant of the solvent. This expression is identical with Kohlrausch's empirical equation.

### Mathematical Derivation of Debye-Huckel Equation

The electrical potential at any point is defined as the work done in bringing a unit charge from infinity to that particular point. Let  $\psi$  be the potential at any given point in the vicinity of a positive ion. Then the work done in bringing a positive ion of valency  $z_+$ , i.e., carrying a charge  $z_+ \epsilon$  ( $\epsilon$  is the electronic charge) to that point is  $z_+ \epsilon \psi$ ; similarly the work required for a negative ion is  $-z_- \epsilon \psi$  where  $z_+$  and  $z_-$  are numerical values only and do not include the sign.

If the concentration of ions at a large distance from the given ion, where  $\psi$  may be taken as zero, are  $n_+^0$  and  $n_-^0$  per unit volume, then by **Maxwell-Boltzmann's Distribution Law** for particles in a field of varying potential, we have

$$n_+ = n_+^0 e^{-(z_+ \epsilon \psi / kT)}$$

$$n_- = n_-^0 e^{-(-z_- \epsilon \psi / kT)}$$

where  $n_+$  and  $n_-$  are the concentrations of positive and negative ions at the given point under consideration,  $k$  is Boltzmann's constant. Since  $z_+$  and  $z_-$  are numericals only, it is clear that  $n_- > n_+$ , i.e., there are, on an average, more negative than positive ions in the vicinity of any positive ion and vice versa. It is seen, therefore, that every ion is surrounded by an oppositely charged ionic atmosphere, that is to say, ions of opposite sign predominate in the ionic atmosphere.

The total charge density,  $\rho_e$  (i.e., charge per c.c.) at any point where the potential is  $\psi$  is given by the excess of positive or negative electricity per unit volume at the point, i.e.,

$$\begin{aligned} \rho_e &= (n_+ z_+ \epsilon) - (n_- z_- \epsilon) \\ &= [(n_+^0 e^{-(z_+ \epsilon \psi / kT)} z_+ \epsilon)] - [n_-^0 e^{-(-z_- \epsilon \psi / kT)} z_- \epsilon] \end{aligned} \quad \dots(7)$$

In a simpler case of a uni-univalent electrolyte,  $z_+ = z_- = 1$ ; and  $n_+^0 = n_-^0 = n$ , where  $n$  is the number per c.c. of ions of either kind in the bulk of the solution. It is seen from (7) that

$$\rho_e = n \epsilon (e^{-\epsilon \psi / kT} - e^{\epsilon \psi / kT}) \quad \dots(8)$$

It is assumed that  $\epsilon \psi / kT$  is small in comparison to unity and so writing the exponential series and neglecting higher powers of  $\epsilon \psi / kT$ , we get from equation (8),

$$\rho_e = -(\epsilon^2 \psi / kT) 2n \quad \dots(9)$$

In the general case when  $z_+ = z_- \neq 1$  and the solution may contain several different kinds of ions. Equation (7) takes the form

$$\rho_e = \epsilon \sum n_i z_i e^{-z_i \epsilon \psi / kT} \quad \dots(10)$$

where  $n_i$  and  $z_i$  represent the number per c.c. and valency, respectively of each kind of ion in turn. If  $z_i \epsilon \psi / kT$  is assumed to be very small as compared to unity, then

$$\rho_e = \sum n_i z_i \epsilon - \sum n_i z_i^2 \epsilon^2 \psi / kT \quad \dots(11)$$

The first term cancels out by virtue of the requirement of overall electrical neutrality, so that equation (11) becomes

$$\rho_e = -(\epsilon^2 \psi / kT) \sum n_i z_i^2 \quad \dots(12)$$



From equation (20), it is evident that the first term  $\frac{z_i \epsilon}{D r}$  is simply the potential at a distance  $r$  due to a single ion of charge  $z_i \epsilon$  in a medium of dielectric constant  $D$ . The second term  $\frac{-z_i \epsilon \kappa}{D}$  is then the potential due to the other ions, i.e., those forming the ionic atmosphere of the given ion. It is this extra potential that is related to the extra free energy of the ionic solution.

A physical significance may be ascribed to  $\kappa$ . The total charge of the ionic atmosphere will be  $-z_i \epsilon$ , since it is equal and opposite to the charge of the central single ion which is  $z_i \epsilon$ . So, if the whole charge of the ionic atmosphere, i.e.,  $-z_i \epsilon$  were placed at a distance  $(1/\kappa)$  from the given ion, the potential produced at it would be equal to  $\frac{-z_i \epsilon \kappa}{D}$ . Therefore,  $\frac{1}{\kappa}$  may be

regarded as the equivalent radius of the ionic atmosphere (fig. 2), i.e., it has the dimensions of length and is called the '**Debye length**' and is of the order of  $10^{-8}$  cm. for ordinary solutions. As seen from equation (16), the actual value of  $\kappa$  depends upon the concentration of the solution and the valencies of the ions. For one molar aqueous solution of uni-univalent electrolyte at  $25^\circ\text{C}$ ,  $\frac{1}{\kappa} = 3.1 \text{ \AA}$ .

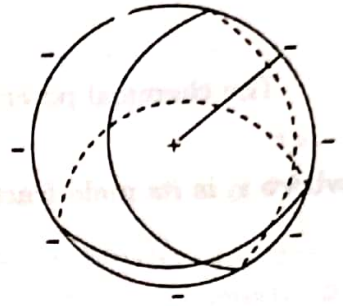


Fig. 2.

The work done in the process of charging i.e., the work done in transferring an ion from infinitely dilute solution to a given solution can be regarded as the difference between the energy required to charge the ion in (i) an infinitely dilute solution and (ii) the given solution.

If the potential at the surface of the ion (radius  $r$ ) at any stage in this process is  $\psi$ , then the work done in bringing up an element of charge  $d\epsilon$  is  $\psi d\epsilon$  and the total work done,  $W$ , in giving the ion its charge  $z_i \epsilon$  is given by the integral

$$W = \int_0^{z_i \epsilon} \psi d\epsilon$$

When the ion has the charge  $\epsilon$ , the potential  $\psi$  at its surface is given by,

$$\psi = \frac{\epsilon}{D r} - \frac{\epsilon \kappa}{D}$$

In an infinitely dilute solution, the second term disappears, since  $\kappa$  is then zero, and the work done,  $W_1$ , in charging the ion is given by,

$$W_1 = \int_0^{z_i \epsilon} \frac{\epsilon}{D r} \cdot d\epsilon = \frac{z_i^2 \epsilon^2}{2 D r}$$

Similarly, the work done,  $W_2$  in charging the ion in the given solution is given by,

$$W_2 = \int_0^{z_i \epsilon} \frac{\epsilon}{D r} \cdot d\epsilon - \int_0^{z_i \epsilon} \frac{\epsilon \kappa}{D} \cdot d\epsilon = \frac{z_i^2 \epsilon^2}{2 D r} - \frac{z_i^2 \epsilon^2}{2 D} \cdot \kappa$$

The work done in transferring the ion from an infinitely dilute solution to the given solution is thus

$$\Delta W = W_2 - W_1 = -\frac{z_i^2 \epsilon^2}{2 D} \cdot \kappa \quad \dots(21)$$

The corresponding energy  $E_i$  for 1 g ion is given by multiplying equation (21) by Avogadro's number  $N$ , so that

$$E_i = -\frac{z_i \epsilon_i^2 \kappa^2}{2D} \cdot N \quad \dots(22)$$

The chemical potential of a particular ion in an ideal solution is

$$\mu_i = \mu^\circ + RT \log x_i \quad \dots(23)$$

where  $x_i$  is its mole fraction in the given solution. For a non-ideal solution, we have

$$\mu_i = \mu^\circ + RT \log a_i \quad \dots(24)$$

$$= \mu^\circ + RT \log x_i + RT \log f_i \quad \dots(25)$$

where  $a_i$  is the activity and  $f_i$  is the activity coefficient. The difference between equations (25) and (23), i.e.,  $RT \log f_i$  is the difference in the free energy change accompanying the addition or removal of 1 g ion of the given ionic species from a large volume of real and dilute solution, respectively. This difference of free energy may be regarded as equivalent to the electrical energy of the ion due to its ionic atmosphere. Hence, from equation (22),

$$RT \log f_i = -\frac{N z_i^2 \epsilon_i^2 \kappa}{2D} \quad \dots(26)$$

or 
$$-\log f_i = \frac{N z_i^2 \epsilon_i^2 \kappa}{2DR T} \quad \dots(27)$$

Now, substituting the value of  $\kappa$  from equation (16),  $n_i$  the number of ions per c.c. may be replaced by  $Nc_i / 1000$ , where  $c_i$  is the number of g ions per litre and  $k$  may be replaced by  $R/N$  and converting the natural logarithm in equation (27) into common logarithm, we get

$$-\log f_i = \frac{A'}{(DT)^{3/2}} \cdot z_i^2 \sqrt{\mu} \quad \dots(28)$$

where

$$A' = \left\{ \frac{N^2 \epsilon^3 \sqrt{2\pi/1000}}{2.3026 R^{3/2}} \right\} \text{ and } \mu = \text{ionic strength}$$

For a given solvent and at a definite temperature,  $D$  and  $T$  are also constant, so equation (28) takes the form

$$-\log f_i = A z_i^2 \sqrt{\mu} \quad \dots(29)$$

where

$$A = A' (DT)^{3/2}$$

Suppose 1 mole of an electrolyte dissociates into  $v$  ions, consisting of  $v_+$  cations and  $v_-$  anions, then we have

$$f_{\pm} = (f_+^{v_+} \cdot f_-^{v_-})^{1/v}$$

or

$$\log f_{\pm} = \frac{v_+ \log f_+ + v_- \log f_-}{v_+ + v_-} \quad \dots(30)$$

If  $z_+$  and  $z_-$  are the valencies of the respective ions we have, by the relationship between the valence and the number of ions,

$$\frac{v_+}{v_-} = \frac{z_-}{z_+}$$

So, introducing this assumption in equation (30), we get



$$\log f_{\pm} = \frac{z_- \log f_+ + z_+ \log f_-}{z_+ + z_-}$$

From equation (29), we get the following for a given solvent at a particular temperature.

$$-\log f_{\pm} = \frac{z_- A z_+^2 \sqrt{\mu} + z_+ A z_-^2 \sqrt{\mu}}{z_+ + z_-} = \frac{A z_+ z_- \sqrt{\mu} (z_+ + z_-)}{(z_+ + z_-)}$$

or

$$-\log f_{\pm} = A z_+ z_- \sqrt{\mu} \quad \dots(31)$$

Equations (29) and (31) represent the Debye-Huckel limiting law, applicable to dilute solutions. According to this law, the temperature of ideal behaviour in a given solvent is governed by the ionic strength ( $\mu$ ) of the medium and the valency of the ions of the electrolytes.